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(54) Title: OPTICAL COMPONENT, ORIENTATION LAYER, AND LAYERABLE POLYMERISABLE MIXTURE

(57) Abstract

In place of separately applied LPP and LCP layers to make an optical component, 7 parts by weight of LCP crosslinkable-diacrylate monomers are mixed with 3 parts of poly(benzopyranoxycarbonyl)ethylene, which itself is linearly photopolymerisable, applied to a substrate, heated to above their isotropic transition temperature, exposed to polarised light, cooled, purged with nitrogen and exposed to light, to make optical components such as retarders or liquid crystal displays.

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**OPTICAL COMPONENT, ORIENTATION LAYER, AND
LAYERABLE POLYMERISABLE MIXTURE**

5 This invention relates to a polymerisable mixture which can be applied as a layer, to an orientation layer of the mixture, and to an optical component (such as a retarder or a liquid crystal display) having a layer of which the mixture is a precursor.

10 Anisotropic transparent or coloured cross-linked polymer layers with three-dimensional orientation of the optical axis, either uniform or preset at individual places, are of great interest in many sectors of display technology, integrated optics etc.

15 For some years, substances having this property in principle have become known, namely certain cross-linkable liquid crystalline diacrylates and diepoxides. Before cross-linking, these substances can be orientated in the liquid crystalline phase in sandwich cells consisting, for example, of glass plates having an interposed monomer layer with the aid of conventional orientating layers on the two glass plate surfaces or under the influence of external fields, e.g. strong magnetic or electric fields, and in a second phase can be photo-cross linked in the cells such that the wall forces acting on 20 the two sides of the monomer layer, or the applied fields, preserve the preset orientation during the cross-linking process.

Cross-linked liquid crystalline monomers or oligomers or polymers are also referred to as LCPs (liquid crystal polymers) in the following text.

25 There have also become known methods which permit the production of orientation layers with locally variable orientating properties.

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U.S. Patent No. 4,974,941 (Gibbons *et al.*) describes a process wherein a preferred direction is induced in response to exposure with linearly polarised light of an appropriate wavelength by the cis-trans-isomerisation of dyes. Liquid crystals in contact with a surface thus exposed are oriented in accordance with this preferred 5 direction. This orientation process is reversible – i.e., by further exposure of the layer to light of a second polarisation direction the orientation direction can be rotated again.

In the case of the photostructurable orientation layers described in U.S. Patent No. 5,389,689 (Chigrinov *et al.*), an irreversible anisotropic polymer network is used. 10 During the exposure to linearly polarised light, anisotropic orienting properties are induced in a photo-polymerisable layer and at the same time a polymer network is built up. Such linear photo-polymerised polymer networks (LPP), also known as photo-oriented polymer networks (PPN), are of use wherever stable, structured or unstructured liquid crystal orientation layers are required.

15 Layer structures comprising an anisotropic film of LCPs in contact with an orientating layer of a linear photo-polymerised polymer network (LPP) are described in U.S. Patent No. 5,602,661 (Schadt *et al.*). The manufacture of these layer structures is effected by orientation of the liquid crystal by interaction with the LPP layer and fixing the 20 orientation in a subsequent cross-linking step. With this technique, it is even possible to manufacture multi-layer structures consisting of several oriented liquid crystal polymer layers, as is shown e.g. in European Application No. 0 689 084 (Schadt *et al.*).

25 As is well known, in addition to an azimuthal alignment, a tilt angle, i.e. an inclination of the optical axis of the liquid crystal layer relative to the plane of the layer, is often necessary. This can be achieved by an LPP orientation layer having a tilt angle on the surface, disclosed e.g. in European Application No. 0 756 193 (Schadt *et al.*).

To sum up, it can be said that LCP layers, usually in combination with orientation layers, are the basis of a large number of optical components like retarders, optical filters, polarizer etc. Layer structures of the type mentioned above with locally varying optical axes can also be used as a safeguard against counterfeiting and copying, as 5 disclosed for example by European Application No. 0 689 065 (Schadt *et al.*).

Furthermore, it is well known to the artisan and understood in the present context that orientation layers are not only used for producing LCP components but also for aligning liquid crystals in liquid crystal displays, light valves etc.

10

The present invention provides and opens up new possibilities both for optical components, particularly of the aforementioned kind, and for liquid crystal orientation layers.

15

According to the invention, a polymerisable mixture comprises

- (i) a liquid crystal monomer or pre-polymer having cross-linkable groups; and
- (ii) a photo-orientable monomer or oligomer or polymer.

20

Despite the distinct functions of the participating molecules, it has been surprisingly discovered that these mixtures are capable of being both oriented and cross-linked into a liquid crystal polymer. These mixtures are hence usable on the one hand as anisotropic layers in optical components or on the other hand, normally applied more thinly, as orientation layers.

25

This leads to various advantages hitherto unavailable.

In the case of an anisotropic layer for an optical component, only one layer need be applied instead of the hitherto necessary two, thus reducing the number of processing steps.

5 In the case of an orientation layer, the orientation proceeds not only at the surface of the layer but can proceed throughout its depth.

It is no longer necessary to apply and appropriately (e.g. imagewise) expose or irradiate an e.g. patterned orientation layer before the LCP layer is applied, in other words the 10 entire layer-applying stage can be completed before the exposure/irradiation stage. These stages can be performed quite independently and even at separate locations. This is an important benefit for security purposes, where a secret alignment pattern is to be imposed on an LPP layer; the manufacturer who applies the LPP layer does not (as hitherto) need to be given the secret pattern, which improves the safeguards against 15 counterfeiting.

Varying the types and proportions of the various chemical components of the mixtures according to the invention is a useful tool for influencing properties such as viscosity and coatability of the mixtures; for example, an unacceptable coalescence into globules 20 of an applied layer of such a mixture can be inhibited by increasing its viscosity.

By "photo-orientable" is meant that the substance (ii) is capable of developing a preferred direction when irradiated with linearly polarised light and thus inducing an alignment of liquid crystals.

25 It is understood that substance (i) may also be an LCP mixture, i.e. may contain two or more different liquid crystal molecule types. Equally, substance (ii) may be a mixture of photo-orientable molecules.

Such a precursor can be manufactured in industrial-sized rolls and transported to the end user (in the dark). The applied layer should be able to withstand the rigours of transport, especially if protected by a peel-off layer.

5 A substrate carrying a layer of a mixture according to the invention, for many applications, should be conductive under the layer.

An optical component according the invention comprises a layer of a mixture as set forth above, in which the liquid crystal monomer or pre-polymer is at least partly 10 polymerised. Such a layer usually will be optically anisotropic.

Preferably, the layer has a preferred orientation direction or locally varying preferred orientation directions, which may be at an angle to the plane of the substrate, in other words with a tilt angle.

15 The thickness of the layer will depend on the use. Thus, for an optical component intended to be used in its own right, such as for instance a retarder, an optical filter, a polarizer or a polarised light emitter, a relatively thick layer, e.g. 0.3 to 5 μm , is preferred. For a layer which is intended to act as an orientation layer without 20 significant inherent optical properties, a thinner coating such as 0.01 to 1 μm is preferred. Although photo-orientable compounds, particularly LPP compounds, can be used by themselves as orientation layers, the LCP compounds may advantageously confer networking forces retaining the preferred direction in the photo-orientable compounds.

25 A method according to the invention of making an at least partly polymerised, optically anisotropic layer of a mixture as set forth above comprises exposing the mixture (preferably in its isotropic phase, e.g. by warming it) to linearly polarised light (optionally in different orientations in different parts of the layer, for example in

imagewise, patternwise and pixellated arrangement) while maintaining such conditions that the polymerisation or cross-linking of substance (i) is essentially inhibited, whereby at least some of the molecules of the substance (ii) are photo-oriented. Initially, the molecules of substance (i), i.e. the liquid crystal prepolymers, must not cross-link.

5 However, once they have adopted the preferred orientation, and there is an adequate proportion of substance (ii) photo-oriented for this eventually to occur spontaneously, the molecules of substance (i) may be polymerised or cross-linked with (polarised or non-polarised) light in the anaerobic conditions (e.g. by purging oxygen with a flow of nitrogen or by vacuum). The differential polymerisation of (ii) then (i) may

10 alternatively be achieved by different wavelengths of exciting radiation, though the preferred method remains adjustment of the oxygen partial pressure.

According to the incident angle of the polarised light, a tilt angle can be built in which the liquid crystal molecules will adopt.

15 Under special conditions, the method may be modified in that the light used for the photo-alignment need not be polarised. If for example the layer is in a cholesteric phase, where the liquid crystal molecules organise themselves in a helical conformation, an alignment of the axes of the helices may be induced by the direction

20 of the incident light.

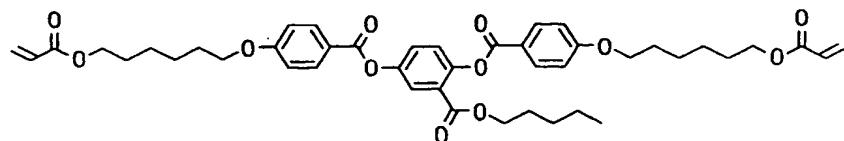
The invention will now be described by way of example.

Example 1

25 Making a solution of an LPP (linear photopolymerisable polymer)/LCP (liquid crystal polymer) mixture

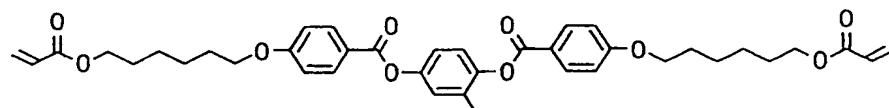
The following photocrosslinkable substances were used to make the LPP/LCP mixture, of which the LCP components, denoted Mon1, Mon2 and Mon3, are crosslinkable diacrylate monomers:

Mon 1:

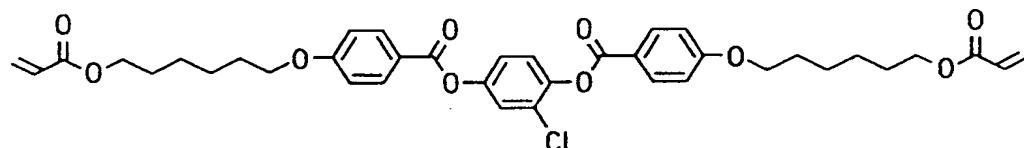


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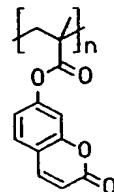
Mon 2:



Mon 3:



LPP A:



10 LPP A was made as described in PCT Publication WO96/10049 Example 1.

Then an LPP/LCP mixture M1 was made from:

54.4 wt% = 224.0mg of Monomer 1

10.2% = 42.2mg of Monomer 2

15 3.4% = 14.2mg of Monomer 3

29.2% = 120.2mg of LPP A

1.4% = 5.6mg of a photoinitiator (Irgacure (trade mark) 369 by CIBA), and
1.4% = 5.6mg of BHT (butyl hydroxy toluene) as an inhibitor.

5 A 5wt% solution of the mixture M1 was made in N-methyl-pyrrolidone (NMP), then
stirred for 30 minutes at 50C, and filtered through a 0.2 μ m filter.

Example 2

Making an Orientation Layer

10 The solution from Example 1 was thinly spin-coated at 2000 rpm onto two ITO (indium-tin-oxide) coated glass plates, which were then dried for 30 minutes at 130C on a hotplate.

15 The dried plates were warmed to 75C and irradiated for 6 minutes under ultraviolet polarised light from a 200W mercury high pressure lamp and having an incident angle of 70°. In this procedure, the direction of polarisation of the light lay in the plane perpendicular to the plate and including the incident light direction. The polariser was a film polariser HNP'B by Polaroid. The wavelength of the light was further limited by a
20 uv filter WG295 (Schott) and a bandpass filter UG11 (Schott). The intensity of the uv light at the plate was determined as 2mW/cm².

After this irradiation, the layers were cooled at 1C/min to 65C, then at 5C/min to 50C. The layers were still liquid.

25 The layers were then irradiated for ten minutes under nitrogen at room temperature by isotropic (not-polarised) light from a mercury lamp at an intensity in the ultraviolet of 4.1mW/cm². Because of the presence of intervening glass (containing the nitrogen), the

incident light no longer included wavelengths below 350nm, which the glass had absorbed.

After this irradiation, the layers were no longer liquid but had become cross-linked.

5

Example 3

Making a parallel-sided cell

10 With the coated sides facing inwards, the two plates from Example 2 were assembled into a parallel-sided cell, using a glass fibre of 20 μ m thickness as a spacer. The cell was immediately filled with a nematic liquid crystal mixture MLC 12000-000 (Merck) at a temperature only just above the liquid crystal-isotropic transition temperature (considered to be 89C in this case), and slowly cooled.

15

Holding the filled cell between crossed polarisers showed that the liquid crystal mixture was uniformly oriented. Using a tilt compensator and a polarisation microscope, the orientation direction which the coated plates had imposed on the nematic liquid crystal mixture was established to be parallel to the direction of polarisation of the uv light
20 which had irradiated the plates.

The rotating crystal technique showed that the tilt angle adopted by the liquid crystal was a hefty 25°.

25 Example 4

Making a solution of an LPP (linear photopolymerisable polymer)/LCP (liquid crystal polymer) mixture

Example 1 was repeated, except that a 25wt.% solution of mixture M1 in NMP was used.

Example 5

5

Coating a Glass Plate

The solution from Example 4 was spin-coated at 1500 rpm onto a glass plate, which was then dried for 10 minutes at 130C on a hotplate. Observation through a polarisation microscope showed that the resulting layer was liquid crystalline but had no preferred orientation. Using a polarising microscope with a hotplate (Mettler FPS) the liquid crystal-isotropic transition temperature was measured as $T_c = 69C$.

Example 6

15

Making an optical retarder layer

The layer from Example 5 was warmed to 75C and irradiated for 3 minutes under ultraviolet polarised light from a 200W mercury high pressure lamp. The polariser was a film polariser HNP'B by Polaroid. The wavelength of the light was further limited by a uv filter WG295 (Schott) and a bandpass filter UG11 (Schott). The intensity of the uv light at the plate was determined as $2mW/cm^2$.

After this irradiation, the layer was cooled at 1C/min to 65C, then at 5C/min to 50C. The layer was then removed from the hotplate and placed between crossed polarisers. The layer was now uniformly oriented. On rotating the substrate, it appeared, alternately, wholly dark or wholly light. Touching it established that the layer was still liquid.

The layer was then irradiated for ten minutes under nitrogen at room temperature by isotropic (not-polarised) light from a mercury lamp at an intensity in the ultraviolet of 4.1mW/cm². Because of the presence of intervening glass (containing the nitrogen), the incident light no longer included wavelengths below 350nm, which the glass had
5 absorbed.

After this irradiation, the layer was no longer liquid but had become firm and cross-linked. Its thickness was 670nm.

10 Using a tilt compensator and a polarisation microscope, the layer was found to have an optical retardation of 52.5nm. It was also established that the orientation of the optical axis all over the layer was parallel to the polarisation direction chosen in the first ultraviolet irradiation.

15 Example 7

Optical retarder layer with tilted optical axis

Example 5 was repeated. Before irradiation, the lower half of the glass plate was
20 covered and the plate rotated 70° about an axis perpendicular to the plane containing the direction of incident light and its direction of polarisation. During irradiation with linearly polarised light, the temperature of the glass plate was held constant at 75C, just as in Example 6. The duration of irradiation was selected to be six minutes, as the effective intensity of the light on the layer was reduced by the rotation of the glass
25 plate.

After this first irradiation, the glass plate was rotated in the opposite direction so that the normal to the substrate surface now made an angle of -70° with the incident direction of the light. Also, now only the upper half of the plate was covered (so that

each half of the plate had only one irradiation). There now followed a second six-minute irradiation, of only the exposed lower half of the plate.

5 Thereafter, as in Example 6, the coating was slowly cooled and, again as in Example 6, was crosslinked under nitrogen with isotropic ultraviolet light.

10 On observing the layer through crossed polarisers, a uniform orientation was apparent, leading to alternate lightening and darkening as the layer was rotated. Using a tilt compensator it was established, as in Example 6, that the optical axis was parallel to the plane of polarisation of the linearly polarised ultraviolet light.

15 The substrate was then so disposed between crossed polarisers that the optical axis made an angle of 45° with the directions of polarisation. On tilting the substrate about an axis which was in the plane of the layer but perpendicular to the optical axis, it could be seen that one half of the layer became darker and the other lighter. Reversing the tilt reversed and inverted the effect.

20 By obliquely illuminating with linearly polarised light, the molecules of the layer were preferentially orientated at an angle to the substrate surface, whereby the optical axis was established with a tilt with respect to the surface.

CLAIMS:

1. An polymerisable mixture comprising
 - (i) a liquid crystal monomer or pre-polymer having cross-linkable groups;
5 and
 - (ii) a photo-orientable monomer or oligomer or polymer.
2. A mixture according to Claim 1, wherein the cross-linkable liquid crystal substance (i) is present in an amount of 100 parts, and the photo-orientable substance (ii) is present in an amount of at least 0.1 part.
10
3. A mixture according to Claim 2, wherein the photo-orientable substance (ii) is present in an amount of at least 1 parts.
15
4. A mixture according to Claim 2, wherein the photo-orientable substance (ii) is present in an amount of at least 10 part.
20
5. A mixture according to any of Claims 1 to 4, wherein the photo-orientable substance (ii) comprises molecules showing a cis-trans-isomerism.
25
6. A mixture according to Claim 5, wherein the photo-orientable substance (ii) comprises azo dyes.
7. A mixture according to any of Claims 1 to 4, wherein the photo-orientable substance (ii) comprises a linearly photo-polymerisable monomer or oligomer or polymer.
25
8. A mixture according to any one of Claims 1 to 7, wherein the cross-linkable liquid crystal substance (I) has a nematic phase.

9. A mixture according to any of Claims 1 to 7, wherein the cross-linkable liquid crystal substance (i) has a cholesteric phase.
- 5 10. A mixture according to any of Claims 1 to 7, wherein the cross-linkable liquid crystal substance (i) has a ferroelectric phase.
11. A mixture according to any preceding claim, wherein the cross-linkable liquid crystal substance (i) is/comprises acrylate or diacrylate.
- 10 12. A mixture according to any preceding claim, further comprising chiral molecules.
13. A mixture according to any preceding claim, further comprising dye molecules.
- 15 14. A mixture according to any preceding claim, further comprising dichroic molecules.
15. A mixture according to any preceding claim, further comprising fluorescent molecules.
- 20 16. A mixture according to any preceding claim, dissolved in a solvent.
17. A presensitised film precursor, comprising a substrate carrying a layer of a mixture according to any of Claims 1 to 16.
- 25 18. A substrate having an electrically conductive surface which carries a layer of a mixture according to any of Claims 1 to 16.

19. An optical component comprising an at least partly polymerised layer of a mixture according to any of Claims 1 to 16.
20. An optical component according to Claim 19, wherein the layer is optically anisotropic.
5
21. An optical component according to Claim 19 or 20, wherein the layer is polymerised with a preferred orientation direction.
- 10 22. An optical component according to Claim 21, wherein the layer is polymerised with locally varying preferred orientation directions.
23. An optical component according to any of Claims 19 to 22, wherein the layer has the function of an orientation layer.
15
24. An optical component according to any of Claims 19 to 22, wherein the layer has the function of a retarder or an optical filter or a polarizer or a polarised light emitter.
- 20 25. An optical component according to any of Claims 19 to 22, wherein the layer has the function of an orientation layer as well as a retarder or an optical filter or a polarizer, or a polarised light emitter.
26. A method of making an at least partly polymerised, optically anisotropic layer of a mixture according to any of Claims 1 to 16, comprising
25
(a) exposing the mixture to linearly polarised light while maintaining such conditions that the polymerisation or cross-linking of substance (i) is essentially inhibited, whereby at least some of the molecules of the substance (ii) are photo-oriented; and

(b) allowing substance (i) to adopt the imposed orientation(s) and exposing the mixture to light, whereby at least some of the molecules of the substance (i) are polymerised or cross-linked.

5 27. A method according to Claim 26, wherein during step (a) the mixture is maintained in its isotropic phase.

28. A method according to Claim 26 or 27, wherein during step (a) the mixture is exposed to light of different directions of polarisation in different parts.

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29. An optical component made by a method according to any of Claims 26 to 28.

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/IB 99/01001

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 G02F1/1337 C09K19/38 G02F1/1335

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G02F C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| Y | | 1,2,6,8, 11,13, 14,17, 18,22,26 |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Int'l. Application No.
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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